

Interfacial Electron Transfer Dynamics of Ru(II)-polypyridine-sensitized TiO₂

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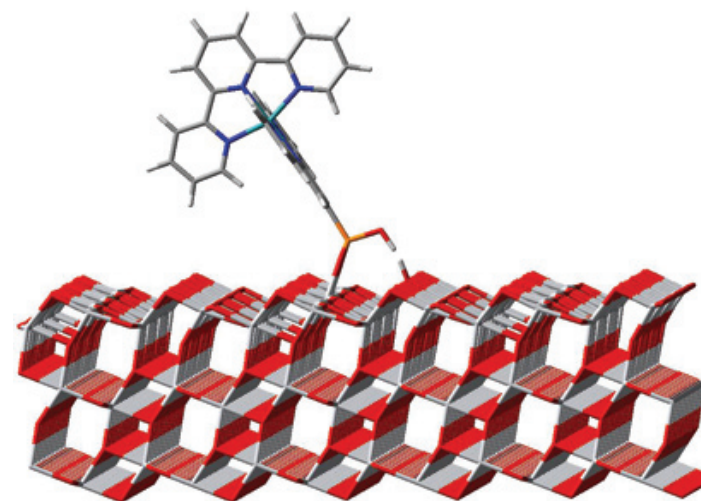
Fig. 1. Ru(tpy)₂ attached to the (101) surface of anatase TiO₂.

Ruthenium polypyridyl complexes are a class of compounds displaying rich photophysics and photochemistry. Due to their favorable excited state properties, they have been widely used in the design of artificial systems capable of converting the energy of light into chemical or electrical energy. In particular, [Ru(tpy)₂]²⁺ is often used in molecular assemblies [1] and dye-sensitized solar cells [2,3] due to its advantageous linear directionality.

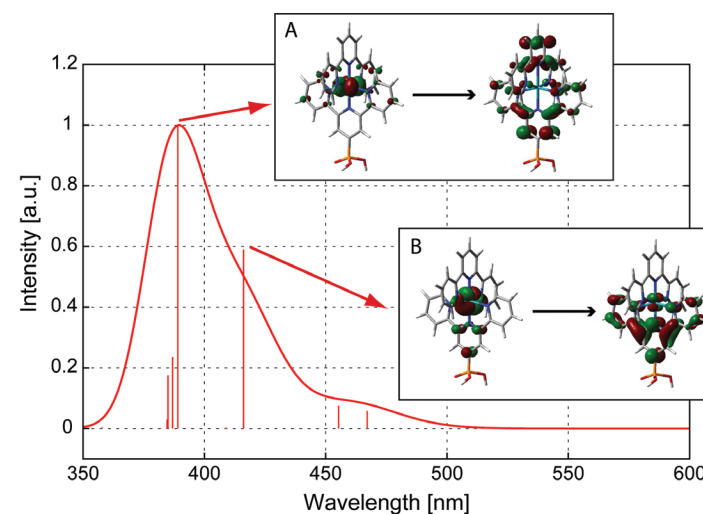
Electron injection from [Ru(tpy)(tpy(PO₃H₂))] ²⁺ adsorbate into TiO₂ will occur upon the excitation of the adsorbate molecule by visible light. Once the adsorbate molecule is in an excited state, several competing processes can occur: 1) radiative or nonradiative transition back into the ground state, 2) intersystem crossing into the lowest triplet excited state, or 3) interfacial electron transfer (IET) from an excited state of the dye into the conduction band of the semiconductor. Intersystem crossing will play an important role in case of the [Ru(tpy)₂]²⁺ molecule, whose lowest triplet excited state has a metal to ligand charge transfer (MLCT) character with a lifetime of 250 ps at room temperature [4].

Density functional theory (DFT) was used to obtain the geometry of the dye-sensitized TiO₂ nanoparticle (see Fig. 1), as well as the absorption spectra and the lowest triplet excited states of the [Ru(tpy)(tpy(PO₃H₂))] ²⁺ dye. Quantum dynamics simulations based on extended Hückel Hamiltonian [5] were then used to study the IET dynamics from the excited states localized on Ru(II) bisterpyridine dye into the nanoparticle. The IET rate was defined as the survival probability $P(t)$, which is the probability that the photoexcited electron remains in the adsorbate molecule at a time t after the excitation.

Fig. 2. Absorption spectra of [Ru(tpy)(tpy(PO₃H₂))] ²⁺ obtained with TD-DFT and natural transition orbitals corresponding to the most intense excitations.



The absorption spectra obtained by the use of time-dependent DFT formalism in the visible region for the free [Ru(tpy)(tpy(PO₃H₂))] ²⁺ molecule are shown in Fig. 2. The two most intense peaks correspond to the excitation of the electron into the orbitals with substantial electron density on the tpy(PO₃H₂) ligand. Natural transition orbitals, which describe these excitations, are also shown in Fig. 2. The excited [Ru(tpy)(tpy(PO₃H₂))] ²⁺ molecule can then undergo



intersystem crossing into the $^3\text{MLCT}$ state, in which the excited electron localizes on the $\text{tpy}(\text{PO}_3\text{H}_2)$ ligand. This state is virtually identical with the $^1\text{MLCT}$ state shown on insert B in Fig. 2.

Density of states (DOS) obtained by the extended Hückel method for $[\text{Ru}(\text{tpy})(\text{tpy}(\text{PO}_3\text{H}_2))]^{2+}$ adsorbed on TiO_2 is shown in Fig. 3. The plot shows the introduction of $[\text{Ru}(\text{tpy})(\text{tpy}(\text{PO}_3\text{H}_2))]^{2+}$ energy levels into the TiO_2 bandgap. Additionally, there are a number of virtual orbitals, LUMO through LUMO + 13 (LUMO = lowest unoccupied molecular orbital), positioned within the conduction band. These are the adsorbate orbitals that are responsible for promoting the IET. The results of the electron dynamics simulations from the four lowest LUMOs are shown in Fig. 4. In general, the IET rate from the adsorbate orbitals with significant electron populations on the $\text{tpy}(\text{PO}_3\text{H}_2)$ ligand is between 1 and 10 ps. Virtual orbitals with the electron population on the terpyridine ligand not attached to TiO_2 and those with the electron population on Ru d orbital do not show significant adsorbate electron population loss in the time scale of our simulations and, therefore, no electron injection into TiO_2 .

In conclusion, we showed that photoexcited $[\text{Ru}(\text{tpy})(\text{tpy}(\text{PO}_3\text{H}_2))]^{2+}$ will inject electrons into the surface of TiO_2 at a competitive rate. The computed injection rate (1 to 10 ps) is faster than the experimental recombination rate (250 ps). Excited states involving electron excitation into the d orbital of Ru or the terpyridine ligand not attached to the TiO_2 surface will not undergo IET into the semiconductor.

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Fig. 3. DOS obtained from the extended Hückel method for the $[\text{Ru}(\text{tpy})(\text{tpy}(\text{PO}_3\text{H}_2))]^{2+}$ -anatase model nanostructure. Shows (a) the valence and conduction bands, and (b) the expanded conduction band. In both plots, the blue line shows the total DOS and the black line represents the projected DOS onto the adsorbate orbitals. The levelset lines give the molecular orbital energies of the free adsorbate in vacuum. DOS is convoluted with a Gaussian function (FWHM = 0.1 eV).

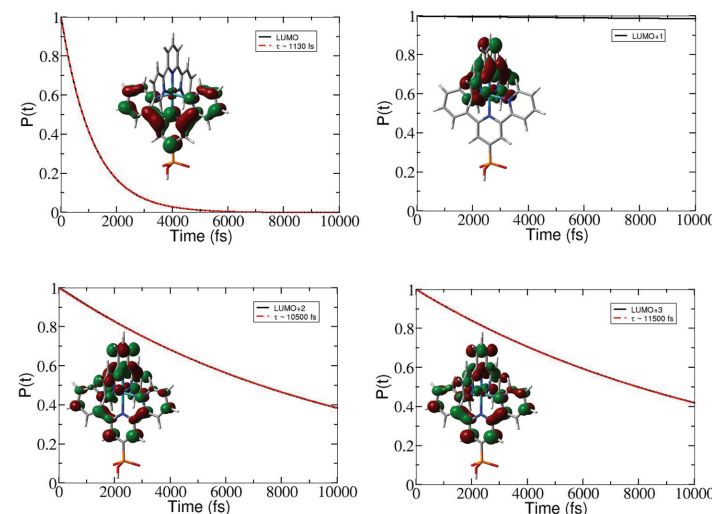
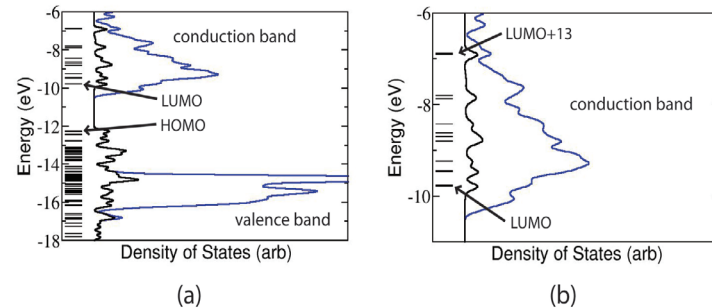


Fig. 4. Survival probability for electron relaxation starting from the LUMO, LUMO + 1, LUMO + 2, and LUMO + 3 virtual orbitals of $[\text{Ru}(\text{tpy})(\text{tpy}(\text{PO}_3\text{H}_2))]^{2+}$ adsorbate. An estimated rate is plotted with the red dashed line.

**Funding
Acknowledgments**
LANL Directed
Research and
Development Program